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A kinetic study of the CH$_2$OO Criegee intermediate self-reaction, reaction with SO$_2$ and unimolecular reaction using cavity ring-down spectroscopy†

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Criegee intermediates are important species formed during the ozonolysis of alkenes. Reaction of stabilized Criegee intermediates with various species like SO$_2$ and NO$_2$ may contribute significantly to tropospheric chemistry. In the laboratory, self-reaction can be an important loss pathway for Criegee intermediates and thus needs to be characterized to obtain accurate bimolecular reaction rate coefficients. Cavity ring-down spectroscopy was used to perform kinetic measurements for various reactions of CH$_2$OO at 293 K and under low pressure (7 to 30 Torr) conditions. For the reaction CH$_2$OO + CH$_2$OO (8), a rate coefficient $k_8 = (7.35 \pm 0.63) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was derived from the measured CH$_2$OO decay rates, using an absorption cross section value reported previously. A rate coefficient of $k_4 = (3.80 \pm 0.04) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was obtained for the CH$_2$OO + SO$_2$ (4) reaction. An upper limit for the unimolecular CH$_2$OO loss rate coefficient of 11.6 ± 0.8 s$^{-1}$ was deduced from studies of reaction (4). SO$_2$ catalysed CH$_2$OO isomerization or intersystem crossing is proposed to occur with a rate coefficient of $(3.53 \pm 0.32) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

Introduction

In 1949 Rudolph Criegee$^1$ proposed that an intermediate (later to be called a Criegee intermediate) was formed during the ozonolysis of alkenes. On addition of ozone to an alkene a primary ozonide (POZ) is formed which decomposes to form a carbonyl and a Criegee intermediate (CI).$^2$–$^4$ Taking ethene as an example, the following reaction sequence leads to the formation of the simplest CI, CH$_2$OO.

\[
\begin{align*}
&\text{H}_2\text{C} = \text{CH}_2 + \text{O}_3 &\rightarrow& \text{H}_2\text{C} = \text{C} = \text{O} \quad \text{(1)} \\
&\text{H}_2\text{C} = \text{O} &\rightarrow& \text{CH}_2\text{O} \quad \text{(2)}
\end{align*}
\]

The Criegee intermediate formed can undergo rapid unimolecular decomposition, often to yield OH radicals,$^3$–$^7$ but a second much slower decomposition has been observed and attributed to so called stabilised CI (SCI).$^6$–$^7$ These SCI are formed with internal energies below the threshold to unimolecular decomposition and are sufficiently long lived to undergo reaction with atmospheric trace gases. SCIs were postulated but remained undetected in the gas-phase until the work of Taatjes and co-workers,$^8$–$^{12}$ who showed that these SCIs could be generated through photolysis of allyl diiodide species in the presence of oxygen, e.g.

\[
\begin{align*}
\text{CH}_2\text{I}_2 + \text{hv} &\rightarrow \text{CH}_2\text{I} + \text{I} &\text{(1)} \\
\text{CH}_2\text{I} + \text{O}_2 &\rightarrow \text{CH}_2\text{OO} + \text{I} &\text{(2)} \\
\text{CH}_2\text{I} + \text{O}_2 + \text{M} &\rightarrow \text{ICH}_2\text{O}_2 + \text{M} &\text{(3)}
\end{align*}
\]

This breakthrough has led to many recent studies that have investigated the UV/visible,$^{13}$–$^{19}$ IR$^{20}$,$^{21}$ and microwave$^{22}$–$^{24}$ spectra, as well as several kinetic studies of CH$_2$OO and CH$_3$CHOO with SO$_2$, NO, NO$_2$, carbonyls, alkenes and organic acids.$^8$–$^{11}$,$^{16}$–$^{25}$–$^{30}$ Direct studies, i.e. ones that monitor the decay of SCI or a proxy of the SCI (e.g. HCHO, OH) return rate coefficients that are considerably larger than previous indirect estimates based on end product analysis.$^2$ These new kinetic data suggest a greater role for SCI species in the atmospheric oxidation of SO$_2$ and NO$_2$ in particular.

Field measurements support a role for the SCI assisted production of H$_2$SO$_4$ (ref. 31) and although model studies disagree as to the extent, they do agree that there is a non-negligible impact of CIs on oxidation of SO$_2$.$^{32}$–$^{34}$ If the gas-phase
oxidation of SO2 to SO3 (and subsequently H2SO4) by SCI competes with, or even dominates in regions of the lower troposphere, over the oxidation by OH, the formation of H2SO4 may be accelerated and aerosol nucleation rates affected.32,33

\[
\text{CH}_2\text{OO} + \text{SO}_2 \rightarrow \text{HCHO} + \text{SO}_3 \quad (4)
\]

\[
\text{OH} + \text{SO}_2 \rightarrow \text{HOSO}_2 \quad (5)
\]

There is considerable debate concerning the impact of these new data, with models predicting effects ranging from significant through to more modest. Given the differences in chemical scheme used in these various model studies as well as model resolution, current disagreement on SCI impact remains to be resolved. However, models that contain detailed chemistries, e.g. the Master Chemical Mechanism35 and its surrogate the Common Representative Intermediates scheme,33 return a more significant impact than those models with less hydrocarbon chemistry.34 A major issue at the core of these discrepancies concerns the two loss processes that dominate the SCI concentration, unimolecular loss and reaction with water vapour:

\[
\text{CH}_2\text{OO} \rightarrow \text{Products} \quad (6)
\]

\[
\text{CH}_2\text{OO} + \text{H}_2\text{O} \rightarrow \text{Products} \quad (7)
\]

Welz et al., Li et al., and Percival et al. noted that significant SCI levels are predicted if \( k_5 \) is around 200 s\(^{-1} \) or less and if \( k_7 \) is less than around \( 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). Further work is required to determine \( k_5 \) and \( k_7 \) more accurately.

Recent work has shown that the rate coefficient for the self-reaction of CH2OO (reaction (8)) is very large.35

\[
\text{CH}_2\text{OO} + \text{CH}_2\text{OO} \rightarrow 2\text{HCHO} + \text{O}_2 \quad (8)
\]

Although this reaction has no atmospheric relevance, it could be important in laboratory studies to probe the kinetics and mechanisms of alkene ozonolysis.36 In this paper we report measurements of \( k_5 \), \( k_6 \), and \( k_8 \) at room temperature over a range of pressure, using near UV cavity ring-down spectroscopy (CRDS) to detect CH2OO. Where appropriate, we compare with previously reported rate coefficients obtained using alternative methods.

**Experimental**

Cavity ring down spectroscopy was used to probe temporal profiles of CH2OO signals in flowing gas samples using the known \( \tilde{B}(1 \text{A}^g) \leftarrow \tilde{X}(1 \text{A}^g) \) electronic absorption band in the near ultraviolet (UV) spectral region. UV probe was generated by frequency doubling the visible radiation output of a dye laser (Sirah CobraStretch, with pyridine 1 dye) pumped by the second harmonic of a Nd:YAG laser (Continuum Surelite III-10). A probe wavelength of 355 nm was chosen to maximize CH2OO absorption and minimize interferences. The ESI† provides detailed discussion of possible interferences and their elimination.

The third harmonic of a Continuum Surelite I-10 Nd:YAG laser (\( \lambda = 355 \text{ nm}; 100 \text{ mJ} \) per pulse; energy density \( \sim 500 \text{ mJ cm}^{-2} \), <10 ns pulse duration) was used to photolyze CH2I2 to start the chemistry leading to production of CH2OO. The unfocused photolysis beam had a diameter of 5 mm with a top-hat intensity profile, and crossed the probe beam (with beam waist of 0.24 mm) at an angle of 5°, giving an overlap length of 5.7 cm in the centre of the CRDS cavity. The delay between the two laser pulses was controlled by a BNC 555 digital delay generator.

High reflectivity mirrors (\( R > 99.9\% \)) at 355 nm, 100 cm radius of curvature were mounted 106 cm apart at opposite ends of a glass tube to form the ring-down cavity. Light escaping from one end of the cavity was monitored by a photodiode (New Focus 1801) and digitized by an 8 bit oscilloscope (LeCroy Waverunner 6030; 350 MHz, 2.5 GSamples per s). Typical ring-down times \( <6 \mu s \) were much shorter than the 1–10 ms timescales used for reaction kinetics measurements under our experimental conditions.

The 6 cm diameter glass tube confined the flow of reagent and bath gases along the detection axis of the spectrometer. The flow rates for all gases were regulated by calibrated mass flow controllers (MKS 1479A and 1179A). The precursor molecule, diiodomethane (CH2I2, 99%), and sulphur dioxide (SO2, \( \geq 99.9\% \)) were purchased from Sigma-Aldrich. CH2I2 was purified further by freeze–pump–thaw cycling before use. High purity nitrogen (N2) and oxygen (O2) were obtained from Air Liquide. Pre-mixtures of CH2I2 in N2 (0.7 Torr/750 Torr) and SO2 in N2 (5 or 750 Torr/1500 Torr) were made and allowed to mix for at least a day to obtain a homogenous mixture. Low flows (20 sccm) of nitrogen were passed through purge lines close to the ringdown mirrors to prevent mirror contamination. All the other gases were passed into the flow tube through a port close to the centre of the cavity. 1.0 to 2.0 Torr of the precursor premixes, 1.0 Torr of oxygen and various pressures of nitrogen were used for the experiments. Sample pressures were measured by two capacitance manometers (0–10 Torr and 0–1000 Torr) located close to the centre of the flow tube. Total flow rates (excluding the mirror purges) ranged from 50–500 sccm, and we verified that the purge flows did not significantly change the overall column length of the gas mixture used in kinetic studies over the total pressure range 7–30 Torr by measuring absorption by CH2I2 or added NO2. We obtained average gas sample lengths of \( 37 \pm 3 \text{ cm} \) that are a factor of 6.5 longer than the overlap region of the photolysis and probe laser beams in which the chemistry of interest occurs. The arrangement of the overlap of the probe and much-larger diameter photolysis laser beams gives a flat concentration profile across the probe region at early times, and diffusion out of the probe volume is expected to be a first order process. We also calculate that mass flow across the probe volume will have negligible effects over the timescales of our kinetic measurements.

Further details of the spectrometer and optimization of experimental conditions are provided in the ESI.†

**Results and discussion**

**I) CH2OO + CH2OO reaction**

Relatively high concentrations of CH2OO need to be produced in laboratory experiments in order to provide enough signal for kinetic measurements. In the present work, typical initial CH2OO concentrations of \( 2.5 \times 10^{12} \text{ molecule cm}^{-3} \) were generated. Under such conditions, the self-reaction can contribute
significantly to the overall loss of CH$_2$OO. Recently, Su et al. reported a CH$_2$OO self-reaction rate constant of $k_8 = (4 \pm 2) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ by monitoring depletion of infrared bands. This value was refined to $k_8 = (6.0 \pm 2.1) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ by Buras et al., by simultaneous monitoring of the near UV band of CH$_2$OO and near IR absorption of iodine atoms. Recently, Ting et al. reported a CH$_2$OO self-reaction rate constant of $8 = (4 \pm 1.0) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ using broadband UV absorption spectroscopy and monitoring CH$_2$OO depletion along with that of CH$_3$I and IO. Reaction of CH$_3$I with O$_2$ was used to produce CH$_2$OO in all of these studies. Using photoionization mass spectrometry, this chemical route was shown to produce sufficient CH$_2$OO radical concentration to perform kinetic measurements. In this work we used a similar reaction pathway shown by reactions (1) and (2) to produce CH$_2$OO. Other than the self-reaction, we also considered the following removal pathways for CH$_2$OO and I.

\[
\text{CH}_2\text{OO} + I + M \rightarrow \text{I} \text{CH}_2\text{O}_2 + M \quad (9)
\]

\[
\text{CH}_2\text{OO} + I \rightarrow \text{IC}_2\text{H}_2 + \text{O}_2 \quad (10)
\]

\[
\text{CH}_2\text{OO} + I \rightarrow \text{HCHO} + \text{IO} \quad (11)
\]

\[
\text{CH}_2\text{OO} + \text{IC}_2\text{H}_2 \rightarrow \text{Products} \quad (12)
\]

\[
\text{I} + \text{I} + M \rightarrow \text{Products} \quad (13)
\]

Under our experimental conditions, CH$_3$I is expected to react with O$_2$ within the first time step (200 µs) of the kinetic measurements. The branching ratio of reactions (2) and (3) determines the yield of CH$_2$OO which increases with a decrease in the concentration of the third body (M). Under low pressure conditions and in the absence of other reactant species, the self-reaction (8), and reactions (9)–(11) with iodine atoms, are expected to be the major loss mechanism for CH$_2$OO. At higher pressures, contribution from reaction (12) will increase. Assuming the fast self-reaction to be the dominant loss mechanism, the decay traces of CH$_2$OO were fitted to an integrated second order decay expression. Further justification for this fitting procedure is provided later. For a second order decay mechanism,

\[
\frac{dN}{dt} = -2k_{\text{obs}}N^2 \quad (14)
\]

in which $k_{\text{obs}}$ is the effective second order decay rate coefficient, $t$ is time and $N$ is the CH$_2$OO concentration. The integrated second order decay rate expression is

\[
N(t) = \frac{N(t_0)}{1 + 2k_{\text{obs}}N(t_0)t} \quad (15)
\]

In eqn (15), $N(t_0)$ is the initial CH$_2$OO concentration. In our cavity-ring down measurements, probe light intensity decay rate constants, $\kappa$, (or ring-down times, $\tau = 1/\kappa$) are measured with and without the photolysis laser on to give a transient absorption signal. The concentration of the absorbing species is given by

\[
N(t) = \frac{\Delta \kappa(t)L}{cda_{\text{355nm}}} \quad (16)
\]

where $\tau_{\text{on}}$ and $\tau_{\text{off}}$ are ring-down times with the photolysis laser on and off, $L$ is the length of the cavity, $c$ is the speed of light, $d = 5.7$ cm is the photolysis and probe laser overlap length, $\sigma_{\text{355nm}}$ is the absorption cross-section of CH$_2$OO at the probe wavelength 355 nm and the change in ring-down rate, $\Delta \kappa$, is directly proportional to the CH$_2$OO concentration. Characterization of the overlap length is presented in the ESI. Combining eqn (15) and (16) gives

\[
\Delta \kappa(t) = \frac{1}{\Delta \kappa(t_0)} + \left( \frac{2}{k_{\text{obs}}L} \right) \kappa'
\]

where $k'$ is the observed second order decay rate coefficient scaled with respect to the CH$_2$OO absorption cross section at 355 nm. Uncertainty in the absorption cross section of CH$_2$OO at the probe wavelength determines the uncertainty in the $k_{\text{obs}}$ value, and as such a cross-section independent value is desired. Thus, the effective second order decay coefficient is expressed in terms of $k'$, which can be readily converted to a second-order rate coefficient for a given choice of value for $\sigma_{\text{355nm}}$.

The ESI summarizes possible sources of interferences at the 355 nm probe wavelength and our procedure for their elimination. The interference-subtracted decay traces were fitted to eqn (18) as exemplified by the data shown in Fig. 1. Data points starting from a 200 µs time delay to around 10 ms were included in the fit. Reaction (2) is calculated to have a half-life of 11.8 µs based on the bimolecular rate coefficient of 1.82 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} (ref. 16) and hence is expected to be complete by 200 µs. Experimental conditions were selected such that the CH$_2$OO signal depletes by greater than 90% by a photolysis-probe delay of 10 ms. Under such conditions, non-second order loss mechanisms like diffusion and mass flow do not contribute significantly to the decay mechanism, as discussed in the Experimental section. Details of the experiments to characterize the non-second order loss mechanisms in the detection region of the flow tube are presented in the ESI.

CH$_2$OO decay traces were obtained for different initial concentrations of the CH$_2$OO (see ESI) and at different bath gas (N$_2$) pressures. Fig. 2 shows the fitted $k'$ values obtained from kinetic decay traces as a function of the bath gas concentration. These values are also provided in Table S4 in the ESI. The quality of the second order fits for the CH$_2$OO decay traces under all the pressure conditions (7 to 30 Torr) is excellent, with adjusted $k'^2$ values greater than 0.99. A second order decay form of the type used in the analysis is strictly valid for a bimolecular reaction in which the two reactants are of equal concentrations. Thus, the extracted $k'$ values should derive primarily from the self-reaction of CH$_2$OO or reaction of CH$_2$OO with similar concentrations of other molecules like ICH$_2$OO, I atom or a mixture of both. The obtained values show a positive
of the pressure dependence evident in Fig. 2 is presented in the 
ESI† and our observations can be accounted for if the rate 
coefficient for reaction of CH$_2$OO with ICH$_2$OO is $k_8 \approx 2 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. This value is consistent with the rate 
coefficient for CH$_2$OO + HO$_2$ of $k = 2.23 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ 
calculated by Long et al.$^{39}$ and is a factor of $\sim 4$ lower than the 
limiting capture rate for a barrierless reaction that we predict from 
estimated dipole moments for CH$_2$OO and ICH$_2$OO.

The zero pressure limit value for $k'$ can therefore be taken as 
an upper limit for the CH$_2$OO self-reaction rate coefficient $k_8$ 
sealed by $\sigma_{355nm}$ (eqn (19)). Table 1 shows the $k_{obs}$ values 
obtained by using the zero pressure limit $k'$ value and the 
$\sigma_{355nm}$values reported by various sources. The CH$_2$OO $\sigma_{355nm}$ 
value from the work of Ting et al. is expected to be the most 
accurate as the CH$_2$OO $\sigma_{355nm}$ value reported in their study is 
similar to the value obtained by Buras et al. using a different 
method. Thus, with incorporation of the quoted uncertainty for 
$\sigma_{355nm}$ values, $k_8 \leq 7.98 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is the best 
estimate for the self-reaction rate coefficient of CH$_2$OO from 
this empirical approach.

To estimate the contributions from reactions (10) and (11) to 
the value of $k_{obs}$, numerical kinetic fits were performed for the 
7 Torr total pressure CH$_2$OO decay trace. This chosen decay 
trace should have minimum contribution from the pressure 
dependent reactions. The I atom self-reaction, (13), CH$_2$OO + I 
reaction and the CH$_2$OO self-reaction, (8), were used in the 
model for the numerical fit. The CH$_2$OO + I reaction takes into 
account the combined effects from reactions (10) and (11) and 
k$_{iodine}$ is taken as its overall rate coefficient. The initial I atom 
concentration was fixed to twice the CH$_2$OO concentration and a 
rate coefficient value of $2.83 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was 
used for reaction (13), obtained using a kinetic rate coefficient 
expression ($M = N_2 = 7$ Torr, $T = 298$ K) reported previously.$^{40}$ 
Fig. 3 shows the results of the fits obtained by varying the $k_{iodine}$ 
values while floating the $k_8$ values. No significant contribution 
from $k_{iodine}$ was found as the fits obtained with the $k_{iodine}$ value 
float and with no contribution from the CH$_2$OO + I reaction 
(i.e. $k_{iodine} = 0$ cm$^3$ molecule$^{-1}$ s$^{-1}$) were identical. The $k_{iodine}$ 
value could not be determined from these fits because the 
dominant removal process for CH$_2$OO is self-reaction ($k_8 > k_{iodine}$) 
under our conditions. The fits obtained by using $k_{iodine}$ values of 
0.5 and $1.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ are of significantly lower 
quality, consistent with the observations of Buras et al. The $k_8$ 
values obtained from these different fits are listed in Table 2.

| Table 1 | Effective second order decay rate coefficient, $k' = k_{obs}/\sigma_{355nm}$, for the loss of CH$_2$OO at the low pressure limit. The values of $k_{obs}$ reported in the fourth column are obtained using $\sigma_{355nm}$ values from various sources |
|--------|----------------|----------------|----------------|
| $k'$ (10$^9$ cm$^{-1}$ s$^{-1}$) | $\sigma_{355nm}$ (10$^{-17}$ molecule$^{-1}$ cm$^2$) | $\sigma_{355nm}$ source | $k_{obs}$ (10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) |
| 6.72 $\pm$ 0.17 | 1.13 $\pm$ 0.05 | Ting et al.$^{18}$ | 7.59 $\pm$ 0.39 |
| 2.5$^a$ | 2.5$^a$ | Beames et al.$^{13}$ | 16.8$^a$ |
| 3.6 $\pm$ 0.9 | 3.6 $\pm$ 0.9 | Sheps$^{16}$ | 24.2 $\pm$ 6.1 |

$^a$ The value of $\sigma_{355nm}$ (with uncertainty on the order of a factor of 2) was obtained from a Gaussian fit to the spectrum reported by Beames et al.
reaction to the overall CH$_2$OO decay is expected to be either similar, or perhaps larger, in the pressure range used in the current work. However, the CH$_2$OO decay profiles obtained in the current study are predominantly second order. Contrary to the observations of Buras et al., we see a definite increase in the effective second order rate coefficient value with pressure, most likely because of contributions from reactions (9) and (12) (see above, and ESI†). These contributions, instead of the CH$_2$OO + I reaction, might cause the decay of CH$_2$OO to assume first-order behaviour with further increase in pressure, and could explain the observations of purely second order CH$_2$OO decay in the current work and the combined first and second order decays of Buras et al. Nevertheless, both approaches should be equivalent in principle to separate the contributions from the self-reaction and other reactions of CH$_2$OO.

Inclusion of the CH$_2$OO self-reaction could be important in the kinetic models for analysis of the end-products of alkene-ozonolysis reactions used to determine the consequences of Criegee intermediate chemistry in the atmosphere. However, the scope of the current work is to obtain bimolecular reaction rate coefficients for the reaction of CH$_2$OO with atmospherically relevant species and inclusion of the overall second order loss of CH$_2$OO in kinetic analysis schemes should suffice. Further detailed discussion of the contribution of the second order loss of CH$_2$OO in the presence of other reagents is presented in the ESI†. Inclusion of the second order loss mechanism will be especially important to characterize accurately the small, but atmospherically relevant, rate coefficients for reactions of CI with species like H$_2$O. Also, in the CH$_2$I$_2$ + O$_2$ synthesis method, the CH$_2$OO second order loss contribution increases with pressure as shown in Fig. 2, and thus should be included in the analysis of experimental results obtained at higher pressures.

\section*{(II) CH$_2$OO + SO$_2$ reaction}

CH$_2$OO oxidizes SO$_2$ to SO$_3$ (reaction (4)) and hence may contribute to atmospheric sulphuric acid production. The bimolecular reaction rate of CH$_2$OO + SO$_2$ has been characterized extensively under low pressure and ambient temperature conditions \textit{via} direct and indirect studies. These reaction rate coefficients have been used to verify the presence of CH$_2$OO and to obtain its near-UV absorption spectrum.\textsuperscript{16} However, direct studies at atmospherically relevant pressures and temperatures are still lacking. This section presents some preliminary work on the effect of extending the pressure range and the inclusion of the self-reaction in the analysis to obtain the reaction rate coefficient of CH$_2$OO with SO$_2$ using the

---

Table 3 Comparison of CH$_2$OO self-reaction rate coefficients, $k_8$, obtained from the current work with previously reported values. Uncertainties incorporate both those from our measurements of $k_8$ at 355nm and the reported uncertainties in $k_8$.

<table>
<thead>
<tr>
<th>$k_8$ (10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.35 ± 0.63</td>
<td>Ting et al.\textsuperscript{35}</td>
</tr>
<tr>
<td>6.0 ± 2.1</td>
<td>Buras et al.\textsuperscript{27}</td>
</tr>
<tr>
<td>40 ± 20</td>
<td>Su et al.\textsuperscript{25}</td>
</tr>
<tr>
<td>8 ± 4</td>
<td>Ting et al.\textsuperscript{38}</td>
</tr>
</tbody>
</table>

---

Table 2 Values for the CH$_2$OO self-reaction obtained from the numerical kinetic fits for different values of $k_{\text{iodine}}$ as shown in Fig. 3.

<table>
<thead>
<tr>
<th>$k_{\text{iodine}}$ (10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$k_8$ (10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00\textsuperscript{a}</td>
<td>9.30 ± 0.09\textsuperscript{a}</td>
</tr>
<tr>
<td>0.00</td>
<td>9.30 ± 0.09</td>
</tr>
<tr>
<td>0.50</td>
<td>8.00 ± 0.11</td>
</tr>
<tr>
<td>1.00</td>
<td>6.85 ± 0.13</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Both $k_{\text{iodine}}$ and $k_8$ were floated in the fit.
directly. It also explores a possible catalytic isomerization or intersystem crossing (ISC) of CH$_2$OO in the presence of low concentrations of SO$_2$ that is proposed to account for some of our experimental observations.

CH$_2$OO decay traces obtained in the presence of SO$_2$ are expected to have contributions from both first and second order loss mechanisms

$$\frac{dN}{dt} = -2k_{\text{obs}}N^2 - k_{\text{pseudo}}N$$

(20)

where, $k_{\text{pseudo}}$ is the pseudo first order rate constant for reaction of CH$_2$OO with SO$_2$ which is present in excess. This rate coefficient can, in principle, also contain contributions from mass flow and diffusion, though these are considered small on the $\lesssim$1 ms timescale of the measurements reported below (see ESI†). The second order contribution is provided by bimolecular reactions of CH$_2$OO, reactions (8), (10) and (11), the overall rate coefficient for which was obtained in the previous section. Eqn (20) is a simple form of Bernoulli’s differential equation, the analytical solution for which is provided in ref. 41.

$$N(t) = \frac{k_{\text{pseudo}}N(t_0)}{k_{\text{pseudo}}e^{k_{\text{pseudo}}t} - 2k_{\text{obs}}N(t_0) + 2k_{\text{obs}}N(t_0)e^{k_{\text{pseudo}}t}}$$

(21)

combining eqn (16) and (21) gives

$$\Delta \kappa(t) = \frac{k_{\text{pseudo}}}{k_{\text{pseudo}} - \kappa' \left( \frac{1}{C_0} \right) + \kappa' \left( \frac{1}{C_1} \right)e^{k_{\text{pseudo}}t}}$$

(22)

The $\kappa'$ values were fixed to the values obtained from the previous section, whereas $\Delta \kappa(t_0)$ and $k_{\text{pseudo}}$ values were floated in the fits. This analysis requires no assumption to be made about the correct value of $\sigma_{355\text{nm}}$. Fig. 4 shows the decays of CH$_2$OO signal in the presence of different concentrations of SO$_2$. The SO$_2$ concentration range used and the robustness of the pseudo first order approximation are justified in detail in the ESI†. These decay traces were fitted to eqn (22) to obtain $k_{\text{pseudo}}$ values for each SO$_2$ concentration. Fig. 5 shows the $k_{\text{pseudo}}$ values as a function of SO$_2$ concentration.

![CH$_2$OO decay traces in the presence of various concentrations of SO$_2$. The initial CH$_2$OO concentration was $\sim 3.3 \times 10^{12}$ molecule cm$^{-3}$. All the decay traces were taken at 10 Torr total pressure. Each individual trace was background subtracted using the method described in the ESI†. The solid lines show the fits performed using eqn (22).](image1)

![CH$_2$OO + SO$_2$ bimolecular reaction rate coefficient as a function of pressure from various sources including the current work. Error bars are 1σ values. The inset key identifies the species monitored in other studies of reaction (4).](image2)

The $k'$ values obtained previously at higher pressures via methods monitoring HCHO$^{28}$ or OH$^{26}$ fluorescence show no dependence on pressure, in agreement with the results obtained of a linear fit gives the CH$_2$OO + SO$_2$ bimolecular reaction rate coefficient.
in this work for pressures from 10–30 Torr. However, the pressure independent \( k_f \) values obtained in this work and from other CH₂OO loss studies are larger than the ones obtained from the more indirect measurements of HCHO or OH production. In the case of the OH fluorescence experiment, OH radicals can form via unimolecular dissociation of CH₂OO, and the \( k_f \) value \((3.53 \pm 0.29) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) was obtained from the linear fit of relatively small pseudo first order rate coefficient values (150 to 250 s\(^{-1}\)). Under such conditions, contributions from the second order reaction of CH₂OO are significant, and correction for this competing pathway for CH₂OO removal should increase the derived \( k_f \) value.

### (III) CH₂OO unimolecular reaction

The unimolecular reaction (6) may be an important loss mechanism for CH₂OO under atmospheric conditions, along with bimolecular reactions with H₂O.33 No rigorous direct experimental study has been performed so far to obtain a CH₂OO unimolecular decay rate coefficient. Fig. 4 and 5 illustrate the pseudo first order analysis performed to obtain bimolecular rate coefficient for the CH₂OO + SO₂ reaction. The intercept value of the linear fit in Fig. 5 should be related to the first order loss of CH₂OO. Unimolecular decay, diffusion and mass flow across the detection axis of the spectrometer could all contribute to the observed first order loss of CH₂OO, but we present evidence in ESI† that the latter two effects are small on the \( \leq 1 \text{ ms} \) measurement times of these experiments. There should not be a significant contribution from wall loss as the radicals are synthesized and probed at the same region in the middle of the 6 cm diameter flow tube.

Second order fits of the CH₂OO decay traces in the absence of SO₂ do not show significant first order contributions, as exemplified in Fig. 1, because of a small first order contribution relative to the dominant second order CH₂OO loss process. However, non-zero intercept values \((>500 \text{ s}^{-1})\) were obtained in the pseudo first order analysis at different total pressures, which appear inconsistent with the fits to second order (self-reaction) decays. To resolve this issue, experiments were performed to obtain CH₂OO decay traces in the presence of lower concentrations of SO₂, more comparable with the CH₂OO concentration.

Fig. 7 shows the CH₂OO decay trace obtained at the lowest SO₂ concentration used in the current work, and the fit using eqn (22) to obtain the first order contribution. Although the pseudo first-order approximation might be expected to break down at the lower end of our SO₂ concentration range, numerical modelling shows that a pseudo first-order treatment remains valid because of the rapidity of the CH₂OO self-reaction. The overall kinetics are still well-described by simultaneous second and first order fits \((\text{adjusted } R^2 > 0.99)\). The inset in Fig. 7 shows the non-linear behaviour of the plot of the reciprocal of \( \Delta v \) as a function of time caused by a first order contribution to the dominant second order decay (CH₂OO self-reaction). Fig. 8 shows the pseudo first order rate coefficients obtained from analysis of the CH₂OO decay traces taken over our whole range of low to high SO₂ concentrations. We see the onset of curvature in the plot for [SO₂] values that are still in more than four-fold excess over the initial concentration of CH₂OO. Separate linear fits were performed for the four highest \((8.64 \times 10^{13} \text{ to } 2.16 \times 10^{14} \text{ molecule cm}^{-3})\) and four lowest \((1.08 \times 10^{12} \text{ to } 6.48 \times 10^{12} \text{ molecule cm}^{-3})\) SO₂ concentrations. The linear fit expressions obtained are \((3.93 \pm 0.13) \times 10^{-11} \times [\text{SO}_2] + 629 \pm 147\) and \((7.46 \pm 0.29) \times 10^{-11} \times [\text{SO}_2] + 11.6 \pm 8.0\) for the high and low SO₂ concentration regimes, respectively.

Fig. 7 CH₂OO decay trace obtained in the presence of low [SO₂] \((1.1 \times 10^{12} \text{ molecule cm}^{-3})\). The initial concentration of CH₂OO was \(~4.9 \times 10^{12} \text{ molecule cm}^{-3}\). The solid lines show the fits performed using eqn (22). The inset shows the reciprocal of the experimental and fitted \( \Delta v \) values as a function of time for clarity. A first order contribution of \(92 \pm 6 \text{ s}^{-1}\) was obtained from this fit.

We hypothesize an SO₂-catalysed but reversible isomerization or ISC mechanism, in competition with reaction to HCHO + SO₃, to explain what we see. A generalized kinetic analysis incorporating the idea is presented in the ESI† and accounts for the observed dependence of \( k_{\text{pseudo}} \) on \([\text{SO}_2]\). Previous theoretical work by Vereeken et al. suggests 17% of the CH₂OO + SO₂ reaction leads to singlet bisoxy radical + SO₂ via a pathway with a submerged energy barrier,10 and this isomerization mechanism is one candidate for our experimental observations. However, we note that the

![Fig. 7](image-url)
reversibility of our proposed mechanism conflicts with the calculations of Vereecken et al. which place the ground states of isomers of CH$_2$OO more than 60 kJ mol$^{-1}$ lower in energy than the Criegee intermediate. An alternative candidate is formation of a triplet state species via intersystem crossing and the calculations of Vereecken et al. lend some support to this suggestion. These authors identified that, in the vicinity of the OCH$_2$OS(O)O biradical adduct of CH$_2$OO and SO$_2$, the singlet and triplet states are split by less than 0.4 kJ mol$^{-1}$; at near degeneracy here or elsewhere in the CH$_2$OO – SO$_2$ configuration space, singlet-triplet mixing may be significant and lead to reversible ISC.

In the absence of an alternative explanation for our experimental observations, we are forced to propose an as-yet unidentified intermediate species such as a triplet biradical, or question the accuracy of the existing calculations, which use single reference methods to describe biradical intermediates that (as the authors themselves argue) would be better treated with multi-reference techniques. Our suggested mechanism remains tentative and clearly is subject to testing if multi-reference electronic structure calculations are performed, or the triplet state reaction pathways are mapped. We therefore do not place undue emphasis on this mechanism here, and further details of our model and analysis instead appear in the ESI.†

The analysis based on our proposed mechanism shows that the pseudo first order rate coefficient at high SO$_2$ concentration can be attributed to bimolecular reaction of CH$_2$OO and SO$_2$, but the intercept of fit 1 depends on both the rate coefficient for unimolecular dissociation of CH$_2$OO in the absence of SO$_2$ and that for the intermediate isomer, as well as the ratio of forward and backward isomerization/ISC reactions. This analysis is supported by numerical fitting, which is also discussed in the ESI.† The intercept value for Fit 1 does not have significant dependence on total pressure (intercept values at pressures, 10 to 30 Torr, are provided in Table S4 in the ESI†) and a pressure independent value of 704 ± 47 s$^{-1}$ was obtained. In the low SO$_2$ pressure regime, our model indicates that the pseudo first order rate coefficient should be the sum of contributions from bimolecular reaction and catalysed isomerization/ISC by SO$_2$, justification for which is provided in the ESI.† A value of (3.53 ± 0.32) × 10^{-11} cm$^3$ molecule$^{-1}$ s$^{-1}$ was obtained for the catalysed isomerization/ISC rate coefficient by subtraction and propagation of errors of the slope values obtained from Fit 1 and Fit 2.

The intercept of the low SO$_2$ concentration fit (Fit 2), 11.6 ± 8.0 s$^{-1}$, is taken as an upper limit for the unimolecular loss of CH$_2$OO in the absence of SO$_2$-induced isomerization/ISC, because it may also contain diffusion and mass flow contributions. Unimolecular rate coefficient values from 100 to 200 s$^{-1}$ have been used previously for atmospheric chemistry modelling of stabilized CH$_2$OO. These values were taken as an estimated upper limit from laboratory based studies of CH$_2$OO. Several recent studies have also reported upper limit estimates for the unimolecular loss rate coefficient around 200 s$^{-1}$. Significant contribution from wall reactions prevented accurate determination of the CH$_2$OO unimolecular loss rate coefficient. Olzmann et al. estimated the CH$_2$OO unimolecular loss rate to be 0.33 s$^{-1}$ based on electronic structure calculations, which is much lower than the estimates from previous kinetic studies using direct sources of CH$_2$OO. The CH$_2$OO unimolecular rate coefficient upper limit value obtained in the current study is more in keeping with the theoretical study. The present study therefore shows that a pathway for CH$_2$OO losses by catalysed isomerization or ISC could bridge the discrepancies between the prior experimental and theoretical estimates.

(IV) Atmospheric implications

SO$_2$ concentrations of 10$^{10}$ to 10$^{11}$ molecule cm$^{-3}$ have been reported in rural and urban environments, respectively. Thus, the CH$_2$OO + SO$_2$ reaction should be in the low pressure limit (for SO$_2$ collisions) in these environments and both the proposed isomerization (or ISC) and bimolecular reaction should be important CH$_2$OO loss pathways. Both of these reactions should also compete with the unimolecular decomposition of CH$_2$OO. Maximum pseudo first order reaction rate coefficients of 12, 1.3 and 1.4 s$^{-1}$ are calculated for the CH$_2$OO unimolecular reaction, the hypothesized SO$_2$-catalysed CH$_2$OO isomerization reaction and CH$_2$OO + SO$_2$ bimolecular reaction using the rate coefficient obtained in this work and a typical atmospheric SO$_2$ concentration of 3.8 × 10$^{10}$ molecule cm$^{-3}$. The lower limiting value for the unimolecular reaction rate coefficient of CH$_2$OO compared with the one used in a previous modelling study should yield a prediction of higher concentration of stabilized CH$_2$OO in the atmosphere.

The CH$_2$OO + H$_2$O and CH$_2$OO + (H$_2$O)$_2$ reactions are expected to be the most important atmospheric CH$_2$OO loss mechanisms. Pseudo first order reaction rate coefficients for the CH$_2$OO + H$_2$O and CH$_2$OO + (H$_2$O)$_2$ reactions could be as high as 36 and 81 s$^{-1}$ based on maximum rate coefficient estimates of 9 × 10$^{-17}$ and 3 × 10$^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and typical atmospheric concentration of 4 × 10$^{17}$ and 2.7 × 10$^{14}$ molecule cm$^{-3}$ for H$_2$O and (H$_2$O)$_2$ respectively. Precise measurements of the CH$_2$OO + H$_2$O and CH$_2$OO + (H$_2$O)$_2$ reaction rate coefficients are needed for more accurate estimates. The work of Leather et al. derived a ratio for $k_6/k_7 = 3.3$ × 10$^{17}$ molecule cm$^{-3}$, and using the upper limit value for $k_6$ obtained in this work leads to an estimate for $k_7 = 3.5$ × 10$^{17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (with a range of 1–6 × 10$^{17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ based on the uncertainty in $k_6$ obtained here). These estimates for $k_5$ are smaller but consistent with the work of Stone et al., and larger than the values used in various studies to estimate urban, regional and global CI levels. Hence, CI levels in these studies may be underestimated, but caution is needed as the rate coefficient for reaction of CI species with water dimers has come under some scrutiny recently and may be sufficiently large to offset this change. Nevertheless, the possibility of significant levels of CI in the boundary layer in particular are supported by this work.

Conclusions

Rate coefficient values for CH$_2$OO self-reaction, reaction with SO$_2$ and unimolecular reaction were obtained at 293 K and...
under low pressure (7 to 30 Torr) conditions using cavity ring-down spectroscopy. Rate coefficient values for the CH$_2$OO self-reaction and reaction with SO$_2$ obtained in the current study are in agreement with previously reported values obtained by different methods. The rate coefficient value for CH$_2$OO unimolecular reaction was found to be significantly lower compared to the estimates from previous experimental studies, but in line with a theoretical estimate. Reversible isomerization or intersystem crossing of CH$_2$OO that is catalysed by SO$_2$ is in line with a theoretical estimate.

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